Pressure effect on the charge-density-wave formation in $2H$-$NbSe_2$ and correlation between structural instabilities and superconductivity in unstable solids

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The hydrostatic pressure dependence of the charge-density-wave onset temperature T_0 in $2H$-$NbSe_2$ was measured up to 20 kbar. dT_0/dP was found to be $-(3.3 \pm 0.2) \times 10^{-4}$ K bar^{-1}. An examination of existing high-pressure data concerning structural instabilities and superconductivity in both layered and isotropic compounds is made.

$2H$-$NbSe_2$ is a trigonal prismatic coordinated layer compound. On cooling, it undergoes a structural transition[1] at the onset temperature $T_0 = 32$ K of a incommensurate charge-density-wave (CDW) state[2] and becomes superconducting below ~7.2 K.[3] The superconducting transition temperature T_0 of $2H$-$NbSe_2$ increases rapidly and nonlinearly with pressure up to ~35 kbar, but slowly and linearly beyond ~35 kbar.[4] This pressure-enhanced superconductivity has been ascribed to the possible suppression of the structural transition by pressure[5] or to the band broadening due to pressure-promoted interlayer coupling[4] (it seems possible that the two are related). Our direct pressure measurements on T_0 show that T_0 decreases with pressure. However, recent results on $2H$-$TaSe_2$ show that pressure increases T_0,[6] and also T_c.[7]

Measurements have been made of the pressure dependences of T_0 and T_c of $2H$-$NbSe_2$ in the fluid mixture of 1:1 n-pentane and isoamyl alcohol, using a self-clamp technique. A sample with a resistance ratio of 30 along the layer between 300 and 8 K was cut from a single crystal grown by iodine chemical vapor transport technique. T_0 is defined as the temperature where the resistance vs temperature curve exhibits a point of inflection. T_0 so defined is slightly lower than that previously obtained[8] at $P = 1$ bar, but gives less uncertainty in determining T_0 at higher pressure. T_c was measured both resistively and inductively. Results are shown in Fig. 1, with the number indicating the sequential order of the experimental runs. The vertical bar for T_0 represents the uncertainty in locating T_0 and that for T_c the transition width. T_0 decreases linearly with pressure up to 20 kbar at a rate of $-(3.3 \pm 0.2) \times 10^{-4}$ Kbar^{-1}. T_c increases with pressure but with a negative curvature. Both T_c and dT_c/dp apparently depend on the measuring technique used, possibly due to the anisotropic nature of the compounds. At atmospheric pressure, $dT_c/dp = +(5.2 \pm 0.1) \times 10^{-5}$ Kbar^{-1}, and $+(4.5 \pm 0.1) \times 10^{-5}$ Kbar^{-1} from resistance and induction measurements, respectively. This latter value is in good agreement with previous observations.[4]

At a second-order transition temperature T_0, the uniaxial stress effect on T_0 is related to the Young's modulus along the ith direction E_i in the following way[9]

$$\left(\frac{dT_0}{d\sigma_i}\right)^2 = -\left(\frac{\Delta E_i}{E_i^2}\right) \frac{T_0}{\Delta C_p},$$

where ΔE_i and ΔC_p are the discontinuities of E_i and the specific heat at the transition. Based on results of the elastic[10] and specific-heat measure-

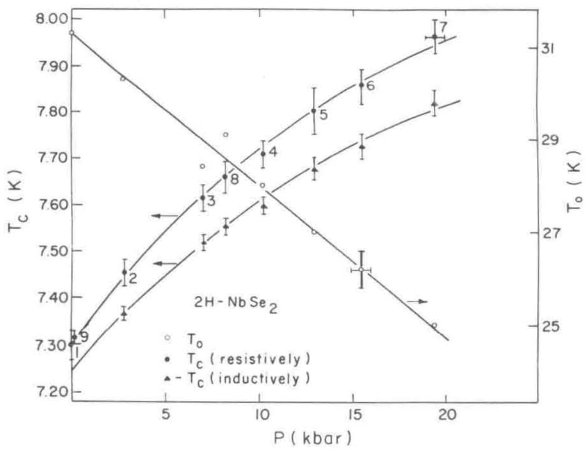

FIG. 1. Pressure dependences of T_0 and T_c of $2H$-$NbSe_2$.

ments,[8] $|dT_0/d\sigma_a| = (6 \pm 2)\times 10^{-4}$ Kbar^{-1} for $2H$-$NbSe_2$ parallel to the layer. Using this value, we deduced the interlayer stress effect $dT_0/d\sigma_c$ to be $-(15 \pm 4)\times 10^{-4}$ or $+(9 \pm 4)\times 10^{-4}$ Kbar^{-1}, depending on whether $dT_0/d\sigma_a$ is positive or negative. The corresponding strain derivative of T_0 is -5×10^2 or $+4\times 10^2$ K for the "+" or "−" sign of $dT_0/d\sigma_a$, based on the estimates of the elastic stiffness constants obtained from neutron and elastic modulus measurements.[11] The interlayer separation thus has a large effect on the CDW formation. The linearly extrapolated critical pressure for the suppression of T_0 to below T_c is larger than 35 kbar. However, the drastic change of dT_c/dP at ~35 kbar can still be related to the suppression of CDW to below T_c, because of the usual nonlinear behavior of T_0 near the critical pressure.[12]

Recently T_0 of $2H$-$TaSe_2$ was observed to increase under hydrostatic pressure up to 19 kbar.[6] The CDW in $2H$-$TaSe_2$ becomes commensurate in a first order transition at $T_d \simeq 90$ K, with a small increase in the CDW amplitude. dT_d/dP is negative,[6] and the critical pressure for the complete suppression of the commensurate state is ~17 kbar.[6] dT_c/dP was determined up to 21 kbar to be positive for the superconducting transition of only a small fraction of the sample. The full transition could not be seen, because the experiment could not be conducted at a lower temperature.[7] However this positive value is consistent with the general trend in dT_c/dP across the $2H$-$TaS_{2-x}Se_x$ system.[7] Therefore the positive dT_c/dP in $2H$-$TaSe_2$ does not seem to be completely accounted for by a possible reduction of the CDW amplitude with pressure due to decreasing T_d.

The effects of pressure on the CDW temperatures T_0 and T_d, and on T_c are known for a number of layer compounds. In general, the three types of phase transitions at T_0, T_d, and T_c are not all observed in the same layer compound, except in the case of $2H$-$TaSe_2$. However, the results in Table I reveal that the pressure coefficients of the three transitions in different compounds at $P = 1$ bar fall into three distinct regions and follow the sequence $|dT_d/dP| > |dT_0/dP| > |dT_c/dP|$, with about an order of magnitude difference between each. This demonstrates that the influence of pressure on a phase transition depends more on the type of transition involved than on the chemical constituents or the polytype of the layer compound. The larger effect of pressure on T_d than on T_0 suggests that the incommensurate-commensurate transition at T_d depends more critically on the band structure of the compound than the normal-incommensurate transition at T_0.

It is interesting to compare the pressure data on layer compounds with those obtained on unstable isotropic superconductors, as shown in Table II. This is especially true of β-W high-T_c compounds, which show structural instabilities, since it has been suggested that these may be due to CDW instability[13,14] (although not yet proven). The magnitude of the pressure dependence of the structural transition temperature T_M in these compounds is similar to that of T_0 in the layer compounds (see Table I). Since T_0 or T_M is always higher than T_c, the relative changes, $|d\ln T_0/dP|$ or $|d\ln T_M/dP|$ and $|d\ln T_c/dP|$ thus become roughly comparable to each other. This is consistent with the propositions[13,15] that structural changes and superconductivity are just two aspects of the same electronic instability. However, one should also note that, in spite of this resemblance, the CDW formation at T_0 in layer compounds differs from the

TABLE I. Pressure effects on T_c, T_0, and T_d. For compounds, in which nonlinear pressure behavior exists, the quoted values are for $P = 1$ bar.

Compound	T_c (K)	dT_c/dP (10^{-5} Kbar^{-1})	T_0 (K)	dT_0/dP (10^{-4} Kbar^{-1})	T_d (K)	dT_d/dP (10^{-3} Kbar^{-1})
$2H$-$NbSe_2$	7.3	+4.95 [a]	31.3	−3.3 [b]	•••	•••
$2H$-$TaSe_2$	0.14	+1.3 [c]	122	+3.5 [d]	92.5	−2.7 [d]
$2H$-TaS_2	0.49	+9.3 [c]	76	−2.2 [e]	•••	•••
$1T$-TaS_2	•••	•••	•••	•••	190	−9 [f]
$1T$-$TaSe_2$	•••	•••	•••	•••	473	−4.7 [g]
$4Hb$-TaS_2	•••	•••	•••	•••	315	−5.5 [h]

[a] Reference 4.
[b] Present work.
[c] Reference 7.
[d] Reference 6.
[e] R. Delaplace *et al.*, J. Phys. Lett. 36 (1976).
[f] C. W. Chu *et al.* (unpublished).
[g] F. J. DiSalvo *et al.*, Solid State Commun. 14, 497 (1974).
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